

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 022 128 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
26.07.2000 Bulletin 2000/30

(51) Int Cl 7: **B32B 27/18**, G02B 5/124,
C08K 5/00, C08K 5/3435

(21) Application number: **99301077.6**

(22) Date of filing: **15.02.1999**

(84) Designated Contracting States
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(72) Inventor: **Phillips, Edward D.**
Oakville, Connecticut 06779 (US)

(74) Representative: **Greenwood, John David et al**
Graham Watt & Co.
Riverhead
Sevenoaks Kent TN13 2BN (GB)

(30) Priority: **20.01.1999 US**

(71) Applicant: **Reflexite Corporation**
Avon, CT 06001-4217 (US)

(54) Extended life fluorescence polyvinyl chloride sheeting

(57) An extended life fluorescent polyvinyl chloride sheeting and a method for forming the sheeting are disclosed. The sheeting includes a polyvinyl chloride film having a fluorescent colorant incorporated therein. A

protective polymer layer is attached to the polyvinyl chloride film. A light filtering agent is incorporated into the protective layer, wherein the filter agent blocks the 425 nm and lower wavelengths of the visible spectrum.

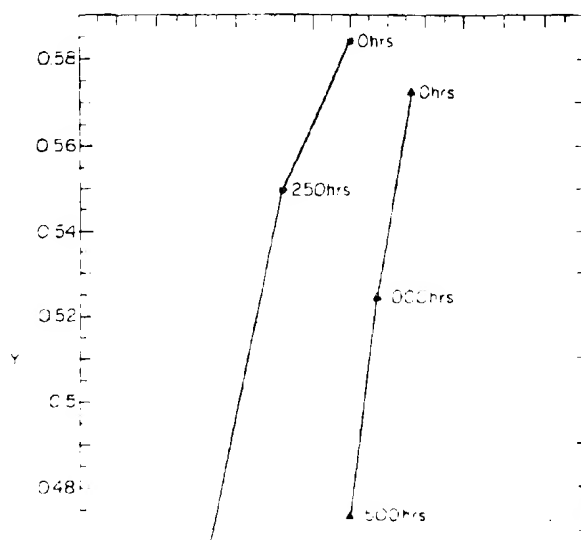


FIG. 1

Description

BACKGROUND OF THE INVENTION

[0001] The advantages of the high visibility of fluorescent materials is well known. However, poor colorfastness in the presence of sunlight has made their use in some applications limited to short-lived, temporary applications. These applications include roadside work zone signs, vehicle conspicuity signs, etc.

[0002] Plasticized polyvinyl chloride has been used extensively for retroreflective sheeting applications. In roadside work zone applications, flexible, roll-up sign age formed of polyvinyl chloride provides an improved safety upon impact by a vehicle over rigid signage. However, the fluorescent colored polyvinyl chloride signs can fade to a clear film quickly after exposure to sunlight as the fluorescent colorant is consumed with lengthy exposure to ultraviolet light emitted by the sun. However, the retroreflective prism structure continues to function.

[0003] Some polymers, such as polycarbonate, that have a fluorescent colorant include a hindered amine light stabilizer compound.

SUMMARY OF THE INVENTION

[0004] The present invention includes an extended life fluorescent polyvinyl chloride sheeting and a method for forming the sheeting.

[0005] The sheeting includes a polyvinyl chloride film having a fluorescent colorant incorporated therein. A protective polymer layer is attached to the polyvinyl chloride film. A light filtering agent is incorporated into the protective polymer layer, wherein the filter agent blocks the 425 nm and lower wavelengths of the visible spectrum.

[0006] The method includes providing a polyvinyl chloride film having a fluorescent colorant incorporated therein. A protective polymer layer is attached to the polyvinyl chloride film. The protective polymer layer includes a light filtering agent that blocks the 425 nm and lower wavelengths of the visible spectrum thereby forming the extended life fluorescent polyvinyl chloride sheeting.

[0007] The present invention has an advantage of providing fluorescent protection to a polyvinyl chloride sheeting while providing solvent resistance, printability, low coefficient of friction and can incorporate water shedding properties such as hydrophobic and hydrophilic.

[0008] Figure 1 is a chart of the results of an accelerated weathering color test of a first sample of the present invention and a first standard product.

[0009] Figure 2 is a chart of the results of an accelerated weathering color test of a second sample of the present invention and a second standard product.

[0010] Figure 3 is a chart of the results of an accelerated weathering color test of the second sample of the present invention and second and third standard products.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention. All percentages and parts are by weight unless otherwise indicated.

[0012] Retroreflective materials are typically formed of a sheet of thermoplastic, which has a colorant mixed therein with the polymers. Attached to the sheet of thermoplastic is an array of cube-corner or prismatic retroreflectors as described in U.S. Patent 3,712,706, issued to Stamm on January 23, 1973. Generally, the prisms are made by forming a master die on a flat surface of a metal plate or other suitable material. To form the cube-corner, three series of parallel equidistant intersecting V-shaped grooves 60 degrees apart are inscribed in the plate. The die is then used to process the desired cube-corner array into a flat plastic surface. When the groove angle is 70 degrees, 31 minutes, 43.6 seconds, the angle formed by the intersection of two cube faces (dihedral angle) is 90 degrees and the incident light is retro-reflected back to the source.

[0013] The efficiency of a retroreflective structure is the measure of the amount of incident light returned within a cone diverging from the axis of retroreflection. A distortion of the prismatic structure adversely affects the efficiency. Furthermore, cube-corner retroreflective elements have low angularity at some orientation angles, for instance, the elements will only brightly reflect light that impinges on it within a narrow angular range centering approximately on its optical axis. Low angularity arises from the inherent nature of these elements which are trihedral structures having three mutually perpendicular lateral faces. The elements are arranged so that the light to be retroreflected impinges into the internal space defined by the faces, and the retroreflection of the impinging light occurs by internal retroreflection of the light from face to face of the element. Impinging light that is inclined substantially away from the optical axis of the element (which is a trisection of the internal space defined by the faces of the element) strikes the face at an angle less than its critical angle, thereby pass-

ing through the face. The master die is used to form a cooperatively configured mold. The prisms are bonded to sheeting which is applied thereover to

provide a composite structure in which cube-corner micropisms project from one surface of the sheeting

[0014] The array of retroreflectors includes optical elements that are known in the art, such as cube-corner prisms, four-sided prisms, Fresnel lenses, rounded lenses, etc. In one embodiment, the array of retroreflectors has a window side and a facet side. The array of retroreflectors are formed of a transparent flexible polymer polyvinyl chloride. Preferably, the polymer is cast in a mold with a monomer or oligomer, and the polymerization is initiated by ultraviolet radiation. Preferably the array of retroreflectors is formed of cube-corner prism elements having a length along each cube side edge in the range of between about 0.003 and 0.02 inches (0.076 and 0.51 mm). In a preferred embodiment, the prism elements have a length along each cube-side edge in the range of between 0.0049 and 0.02 inches (0.124 and 0.51 mm). In a particularly preferred embodiment, each cube-side edge has a length of about 0.0049 inches (0.124 mm).

[0015] An adhesive can be applied to the prism facets for attaching a backing layer to the retroreflective structure. If an adhesive is employed on the prism facets, the adhesive can cause the surface of the prisms to wet, thereby destroying the air interface and eliminating the ability of the prism to retroreflect. As a result, the reflective coating is preferably deposited on the surface of the dihedral facets. Typically, the reflective coating is formed by sputtering aluminum, silver or gold or by vacuum metalization. Alternatively, metal lacquers, dielectric coatings and other specular coating materials can be employed.

[0016] The retroreflective structure 24 can be formed by numerous methods. Some of the methods for forming a retroreflective structure are disclosed in U.S. Patent 3,684,348, issued to Rowland on August 15, 1972; U.S. Patent 3,689,346, issued to Rowland on September 5, 1972; U.S. Patent 3,811,983, issued to Rowland on May 21, 1974; U.S. Patent 3,830,682, issued to Rowland on August 20, 1974; U.S. Patent 3,975,083, issued to Rowland on August 17, 1976; U.S. Patent 4,332,847, issued to Rowland on June 1, 1982; U.S. Patent 4,801,193, issued to Martin on January 31, 1989; U.S. Patent 5,229,882, issued to Rowland on July 20, 1993; U.S. Patent 5,236,751, issued to Martin *et al.* on August 17, 1993; U.S. Patent 5,264,063, issued to Martin on November 23, 1992; U.S. Patent 5,376,431, issued to Rowland on December 27, 1994; U.S. Patent 5,491,586, issued to Phillips on February 13, 1996; U.S. Patent 5,512,219, issued to Rowland on April 30, 1996; U.S. Patent 5,558,740, issued to Bernard *et al.*

zone, vehicle conspicuity, etc., limited to short-lived, temporary applications

[0018] Plasticized vinyl has been used extensively for retroreflective sheeting applications. In applications, such as roadside work zones, it has also been well established that flexible so-called "roll-up" signage usually made of highly plasticized polyvinyl chloride provide greatly improved safety upon impact over rigid signage.

[0019] The use of a free radical absorber of the hindered amine light stabilizer type, such as 2,2,6,6-tetramethylpiperidine, has been used to improve the colorfastness of polycarbonate colored with the thioxanthone, perylene imide, and thioindigold fluorescent colorants (U.S. Patent 5,605,761)

[0020] It has been found that by use of a protective polymer layer or coating or film layer made of polyacrylate, polyurethane, or polyurethane acrylates which incorporate ultraviolet absorbers of the benzophenone or benzotriazole-type along with a light filtering agent which blocks out the short wavelengths of the visible spectrum (425 nm and lower) over a highly plasticized flexible fluorescent polyvinyl chloride sheeting containing a suitable hindered amine, colorfastness can be greatly improved. The wavelengths of visible light extend between about 400 nm for the extreme violet and about 720 nm for the deep red. The visible light filtering agent should impart color that can obscure the desirable daytime visibility of the fluorescent product. A suitable visible light filtering agent is Color Index Solvent Yellow 93. A suitable amount of filtering agent is in a range of between about 0.05 and 5.0 percent. A preferred range is between about 0.1 and 1.5 percent. A suitable hindered amine for use with polyvinyl chloride is bis-(1,2,2,6,6-tetramethyl-4-piperidinyl) sebacate. A suitable amount of hindered amine is in a range of between about 0.1 and 7.0 percent. A preferred range is between about 0.2 and 1.5 percent.

[0021] Through selection of coating ingredients in the top coat protective polymer layer, the fluorescent protection features can be coupled with a wide variety of different performance properties including but not limited to cold temperature flexibility, solvent resistance, printability, low coefficient of friction, and specialized water shedding properties (i.e. hydrophobic hydrophilic)

[0022] The colors of principal interest in the area of fluorescent retroreflective sheeting are lime-yellow and red-orange

[0023] The base material of wavelength filtering layer can be a polymer film, such as polyvinyl chloride, polyacrylate, polyurethane, polyvinylidene chloride, fluor-

[0017] The use of a wavelength filtering layer in the presence of ultraviolet light has made the use in some important applications, such as roadside work

zone, vehicle conspicuity, etc., limited to short-lived, temporary applications. The wavelength filtering layer can be in the range of between about 0.1 and 10 mils (0.00254 and 0.254 mm)

The base material of the wavelength filtering layer can also be applied to the fluorescent colored layer as a coating. This coating can be solvent borne, water-based, two-part, or radiation curable in nature.

[0024] The wavelength filtering layer is protective to the colorant in the fluorescent colored layer by incorporation of ultraviolet light absorbers or selected colorants or both which can block the wavelengths that are destructive to the colorant but still allow the day bright color to be visible. The daytime visibility of the product can be temporarily enhanced by the incorporation of some fluorescent colorant into the wavelength filtering layer, provided that the wavelengths generated by fluorescent colorant in the filtering layer are not destructive to the primary fluorescent colorant in the fluorescent colored layer.

[0025] For the fluorescent colored layer, a base polymer of polyvinyl chloride is preferred. Incorporated into this layer is the primary fluorescent colorant of the product. The most commonly used, widely available, and lowest cost fluorescent colorants are the xanthene based fluorescent dyes. This group, which encompasses both the fluorenes and the fluorones, includes such as dyes as fluoresceins, rhodamines, eosines, phloxines, uranines, succineins, sacchareins, rosamines, and rhodols. The dyes are noted for their brilliant daytime colors, high intensity color compatible fluorescence, and poor light fastness. Other fluorescent dyes displaying better light fastness include pyranines, anthraquinones, benzopyrans, thioxanthenes, and the perylene imides.

[0026] The prism layer can be compression molded or cast directly onto the fluorescent colored layer or attached by means of a tiecoat. The prism layer can be formed of polyvinyl chloride, an acrylate or other suitable polymers.

[0027] This prismatic sheeting configuration can be sealed to any number of backing materials by radio frequency, thermal, or sonic welding methods. The daytime color saturation (chroma) properties of a transparent fluorescent material are increased if backed by a white layer. It is desirable to have the backing be white in color on the surface behind the prisms. Alternatively, the prismatic material can be aluminum metalized in an aesthetically appealing pattern and laminated to a white pressure sensitive substrate adhesive. Similarly, a pattern can be printed onto the film prior to casting, or onto the backs of the prisms after casting, using a white ink to enhance the daytime chroma. However, these methods enhance the daytime fluorescent color at the expense of some of the retroreflective area, because the

gap can help augment the physical durability of the sheeting, because each layer of the product has about 100% of its surface bonded to its adjacent layers.

[0029] If a reflective material that is environmentally stable yet whiter than aluminum can be coated onto the prism facets, it can allow a fully metalized product to have an adequate "cap Y" to produce a desired daytime color. Silver, chromium, gold, palladium, and platinum are also possibilities.

[0030] The product can conform to the Minnesota Department of Transportation Specification 1710 for Fluorescent Orange Retroreflective Sheeting for Use on Work Zone Traffic Control Devices. It defines a color box (see Product Testing Requirements and Specification section), reflectance limits (30 minimum new, 20 minimum to 45 maximum for weathered (500 Weatherometer hours)), and a table (B) of Minimum Coefficients of Retroreflection approximate the 1,300 hour color retention in a xenon lamp accelerated weathering device.

[0031] A series of test samples was prepared for accelerated weathering testing under ASTM G26.

Example 1

[0032] A fluorescent lime (yellow-green) colored microprismatic product was formed having a polyvinyl chloride base film. The polyvinyl chloride base film was highly plasticized using phthalate monomeric plasticizers and a xanthene solvent yellow as a colorant with a benzophenone ultraviolet absorber additive having a thickness of about 250 μ thick. The film was further protected with a 7 μ thick topcoat based on a flexible urethane acrylate oligomer, and containing a benzotriazole ultraviolet absorber and a hindered amine light stabilizer, and C.I. Solvent Yellow 93. This configuration of polyvinyl chloride and additives absorbed eighty-five percent or more of the light having wavelengths of 450 nm and shorter.

Example 2

[0033] A fluorescent orange colored microprismatic product was formed having a polyvinyl chloride base film. The 350 μ thick polyvinyl chloride base film was highly plasticized using phthalate monomeric plasticizers and colored with a fluorescent orange, thioxanthone colorant, a benzophenone ultraviolet absorber additive, and hindered amine light stabilizer. The film was further protected with a clear, 100 μ thick, polyvinyl chloride based top film containing a benzophenone ultraviolet absorber additive.

[0028] Another alternative construction of a film may have the advantage of not having an air gap in the construction behind the prism layer. Elimination of the air

[0034] Another alternative construction of a film may have the advantage of not having an air gap in the construction behind the prism layer. Elimination of the air

plasticizers and a mixture of a xanthene solvent yellow and rhodamine B as colorants

Example 4

[0035] A fluorescent orange colored microprismatic standard Product B was formed having a polyvinyl chloride base film. The polyvinyl chloride base film is highly plasticized using phthalate monomeric plasticizers. The film was made from a lamination of two 150 μ thick polyvinyl chloride films. The first polyvinyl chloride film included a non-fluorescent but very light stable combination of a transparent diazo yellow and organic red pigments. The second polyvinyl chloride film included the highly fluorescent but comparatively fugitive combination of colorants used in Standard Product A.

Example 5

[0036] A fluorescent lime (yellow-green) colored microprismatic standard Product C was formed having a polyvinyl chloride base film. The 250 μ thick, polyvinyl chloride base film was highly plasticized using phthalate monomeric plasticizers and a xanthene solvent yellow colorant.

[0037] All of the aforementioned Examples 1-5 included the same microprismatic array composed of a cross-linked acrylated urethane ester. Each of the prismatic films was sealed by radio frequency welding to a polymeric plasticized, opaque white, textured, polyvinyl chloride backing material for purposes of this accelerated weather testing

[0038] All of the samples were mounted onto an aluminum panel with pressure sensitive adhesive and tested in an Atlas model C35 Xenon Weatherometer in accordance with the ASTM G26 test method for a total of 1,500 hours. The samples were evaluated periodically throughout the duration of the test for color change using a HunterLab LabScan II, LS-6000 Spectrophotometer.

[0039] Minimal movement in color coordinates can show color stability. The orange colorant in a standard product can fade to yellow (out of the color box) after approximately 48 hours in a carbon-arc Weatherometer while the orange colorant in a sample of the present invention can still be in the color box after fifteen hundred hours of exposure. An example of a color box is shown in Figure 2 as defined by the orange color region boundary (Coordinate 1, x=0.550, y=0.360; Coordinate 2, x=0.630, y=0.370; Coordinate 3, x=0.581, y=0.418; Coordinate 4, x=0.516, y=0.394). The color box coordinates are disclosed in ASTM D4956-95, Table 10 for Color Specification Limits (Daytime) for white, yellow,

[0040] Figure 1 shows the degree of color change (distance moved) in CIE 1931 standard color space for Standard Product C (described in Example 5) after 375 hours of testing was greater than the sample described in Example 1 after 1,500 hours of exposure testing. The date point labels indicate hours of exposure in the Weatherometer

[0041] Figure 2 shows the rapid color change of fluorescent orange Standard Product A (as described in Example 3) after only 100 hours of exposure which resulted in a change in color from orange (0.595, 0.4) to yellow (0.498, 0.47) as compared to the color stability of a sample of the present invention, as described in Example 2, after 1,500 hours of exposure, which maintained its orange color.

[0042] Figure 3 shows the colorfastness performance of two commercially available products compared to the present invention as described in Example 2. Standard Product B (Example 4) exhibited rapid color change over the first 125 hours of exposure as the conventional fluorescent colorants faded and then became fairly stable between 125 hours and 1,500 hours when the non-fluorescent pigments are responsible for the color. The Standard Product C (Example 5) also demonstrated a greater over all color change than the embodiment of Example 2. A more significant fact is that the Standard Product C color loss direction indicates a more significant decrease in chroma (shift to the left). This loss of color saturation in the standard Product C (Example 5) indicates that the embodiment of Example 2 can have better visibility in real world daytime applications.

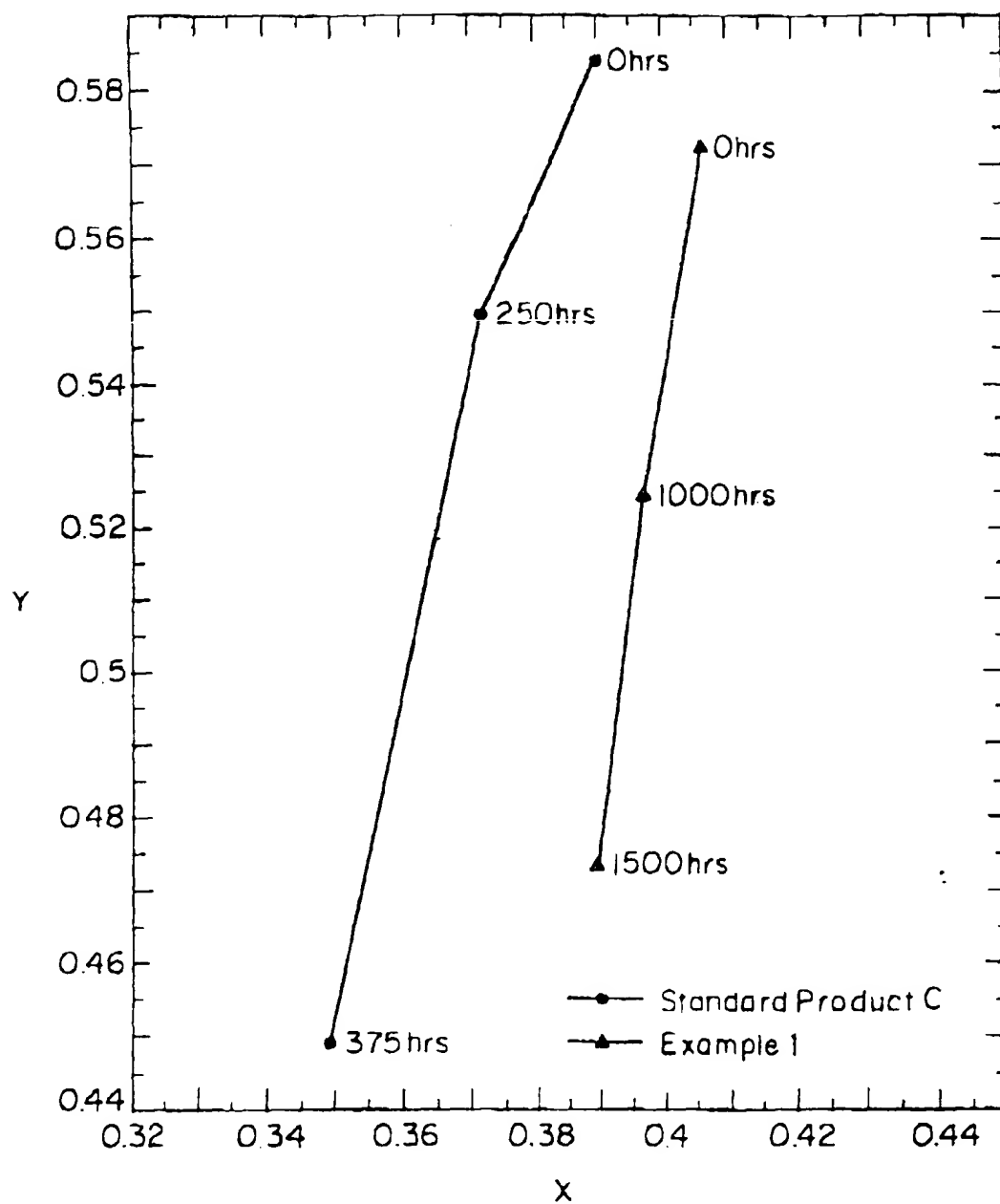
Claims

1. An extended life fluorescent polyvinyl chloride sheeting, comprising
 - a) a polyvinyl chloride film having a fluorescent colorant and hindered amine light stabilizer incorporated therein
 - b) a protective polymer layer which is attached to said polyvinyl chloride film; and
 - c) a light filtering agent, which is incorporated into said protective layer, said filtering agent blocks the 425 nm and lower wavelengths of the visible spectrum.
2. The sheeting of Claim 1 wherein said protective layer includes an ultraviolet absorber
3. The sheeting of Claim 1 wherein said filtering agent includes Color Index Solvent Yellow 69

responding to the CIE 1931 standard Colorimetric system by standard Illuminant C

5. The sheeting of claim 1 wherein said protective polymer layer includes a polymer selected from the group consisting of polyacrylate, polyurethane, polyurethane acrylate, polyvinyl chloride, polyvinyl acetate and polyvinylidene chloride 5
6. The sheeting of Claim 2 wherein said ultraviolet absorber is selected from the group consisting of benzophenone and benzotriazole 10
7. The sheeting of Claim 1 wherein said protective layer has a thickness in the range of between about 5 and 381 micrometers (0.2 and 15 mils).
8. The sheeting of Claim 1 wherein said protective layer has a thickness in the range of between about 12.7 and 25.4 micrometers (0.5 and 1.0 mil) 15
9. The sheeting of Claim 1 wherein said polyvinyl chloride film includes a printed pattern 20
10. The sheeting of Claim 9 wherein said polyvinyl chloride film includes a printed pattern formed of a white ink to enhance daytime chroma. 25
11. The sheeting of Claim 1 wherein the polyvinyl chloride film includes a metalized layer.
12. The sheeting of Claim 11 wherein the metalized layer is formed of a metal selected from the group consisting of aluminum, chromium, gold, palladium, platinum and silver. 30
13. A retroreflective structure formed with the fluorescent polyvinyl chloride sheeting of Claim 1. 35
14. A method for forming an extended life fluorescent polyvinyl chloride sheeting, comprising the steps of:
 - a) providing a polyvinyl chloride film having a fluorescent colorant incorporated therein; and 40
 - b) attaching a protective polymer layer to said polyvinyl chloride film wherein said protective polymer layer includes a light filtering agent that blocks the 425 nm and lower wavelengths of the visible spectrum, thereby forming the extended life fluorescent polyvinyl chloride sheeting. 45

50



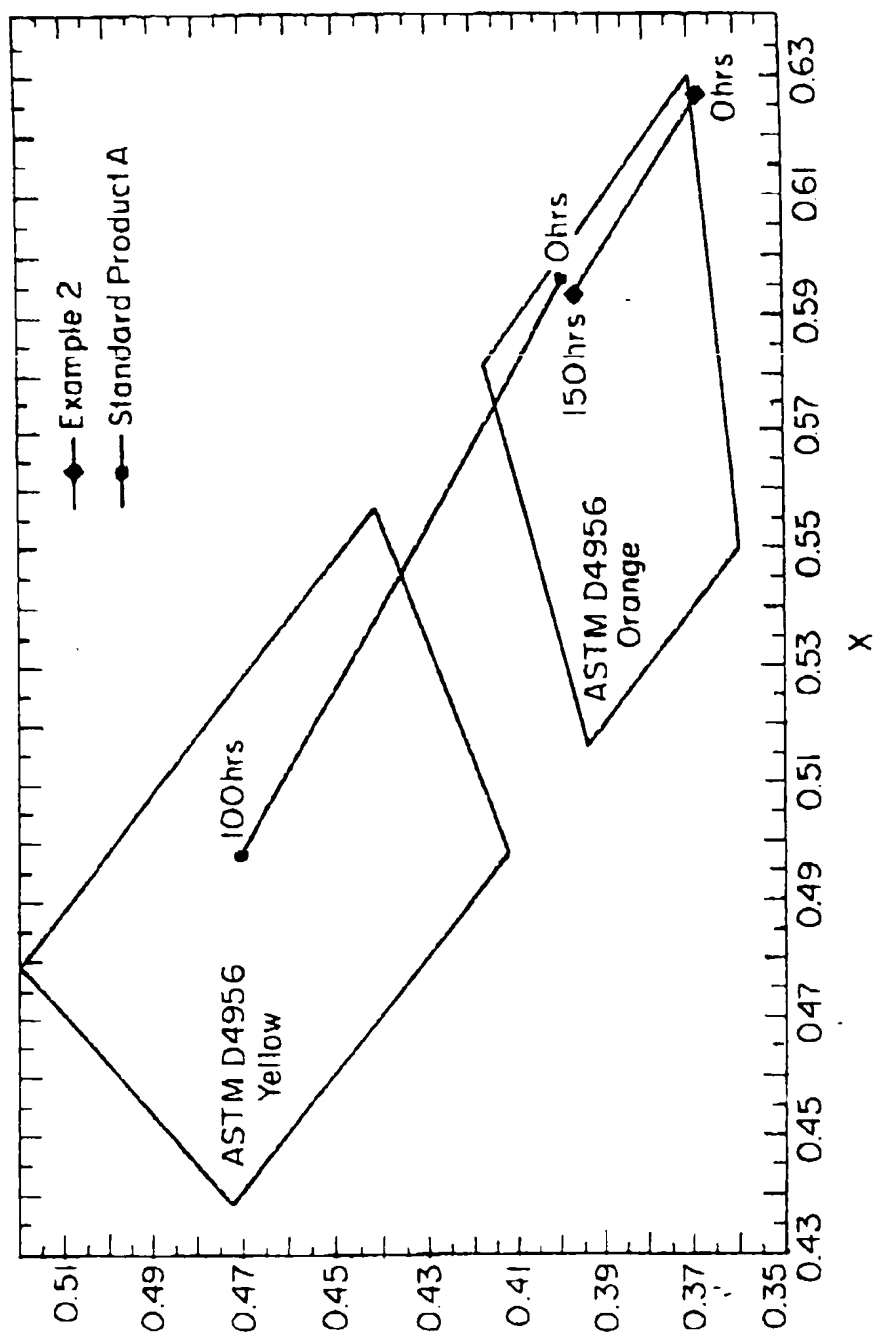


FIG. 2

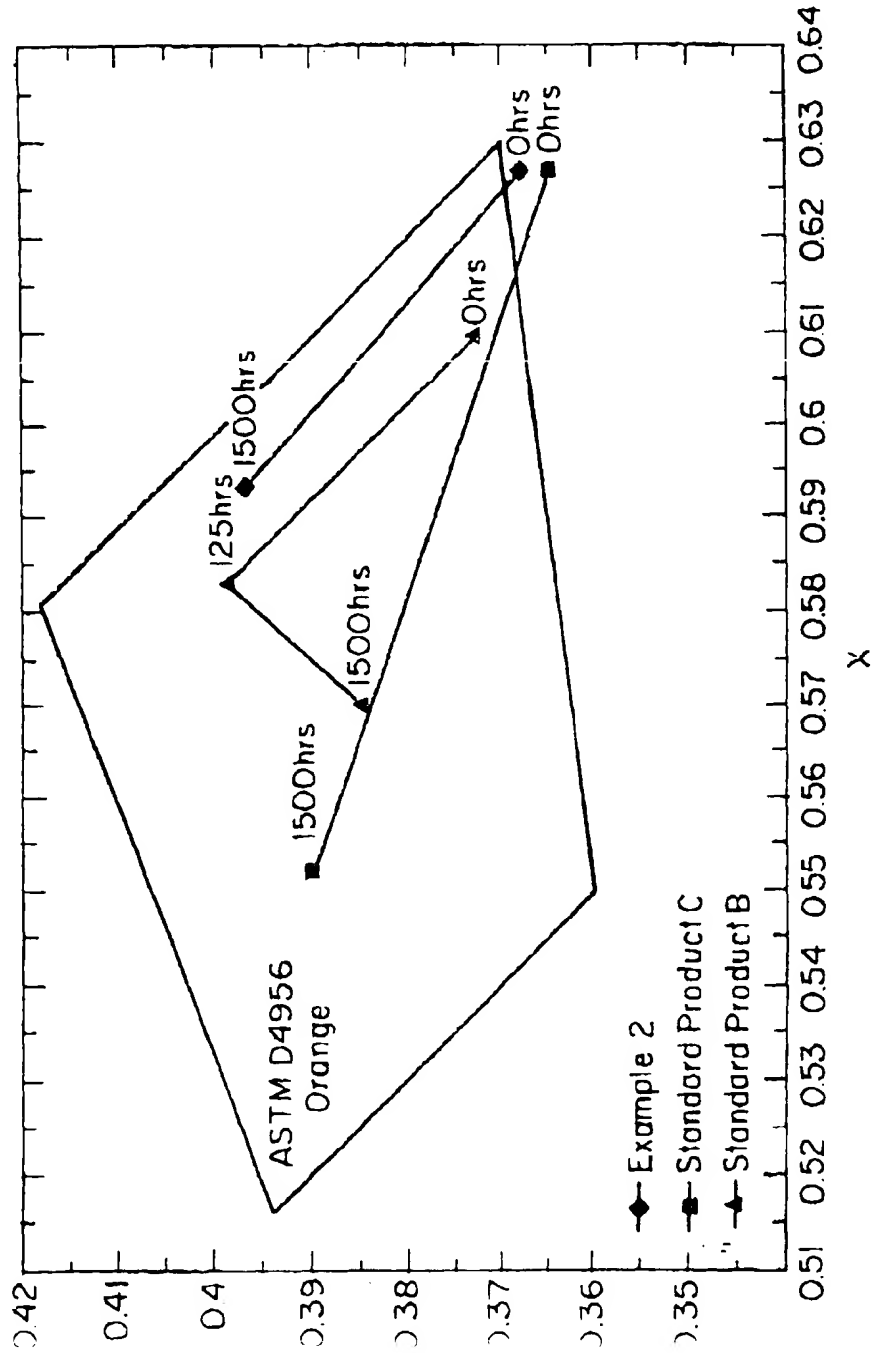


FIG. 3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 30 1077

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	WO 97 37252 A (REFLEXITE CORP) 9 October 1997	1,2,5, 11-13	B32B27/18 G02B5/124
Y	* page 5, line 33 - page 6, line 2-14-35: claims 1,5,7,8,13,15,18; figures 1,2 *	3,14	C08K5/00 C08K5/3435
D,Y	US 5 605 761 A (BURNS DAVID M ET AL) 25 February 1997	1,2,5, 11-13	
Y	* column 4, line 40; tables 8-10 *	3,14	
Y	EP 0 599 208 A (ROEHM GMBH) 1 June 1994	1,2,5, 11-13	
Y	* claim 1 *	3,14	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B32B G02B C08K
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		18 May 1999	Derz. T
CATEGORY OF CITED DOCUMENTS		T: theory or principle underlying the invention	

42 (P.3/201)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 30 1077

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

18-05-1999

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9737252	A	09-10-1997	NONE	
US 5605761	A	25-02-1997	AU 700888 B	14-01-1999
			AU 3834195 A	19-06-1996
			CN 1168684 A	24-12-1997
			EP 0794975 A	17-09-1997
			JP 10510313 T	06-10-1998
			WO 9617012 A	06-06-1996
			US 5816238 A	06-10-1998
EP 0599208	A	01-06-1994	DE 9216001 U	14-01-1993
			AT 149015 T	15-03-1997
			DE 59305491 D	27-03-1997
			DK 599208 T	21-04-1997
			ES 2099885 T	01-06-1997
			JP 6206286 A	26-07-1994